Lead

★Method 8033 — Dithizone Method[1]

Powder Pillows — (3 to 300 µg/L)

Scope and Application: For water and wastewater; USEPA accepted for reporting for wastewater analysis (digestion is required).[2]

[1] Adapted from Snyder, L. J., Analytical Chemistry, 19 684 (1947).

[2] Procedure is equivalent to Standard Method 3500-Pb D for wastewater analysis.

Test Preparation

Before starting the test:

For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water instead of the sample.
Clean all glassware with a 1:1 Nitric Acid Solution. Rinse with deionized water.
Cloudy and turbid samples may require filtering before running the test. Report results as µg/L soluble lead. Use glass membrane type filter to avoid loss of lead by adsorption onto the filter paper.
If samples cannot be analyzed immediately, see Sample Collection, Preservation, and Storage on page 5. Adjust the pH of preserved samples before analysis.
For more accurate results, adjust the sample to pH 11.0–11.5 using a pH meter in Step 10. Omit the five additional drops of Sodium Hydroxide Standard Solution in Step 11
The DithiVer powder will not completely dissolve in the chloroform. For further notes see DithiVer Solution Preparation, Storage, and Reagent Blank on page 5.
Read the MSDS before testing. Spilled reagent will affect test accuracy and is hazardous to skin and other materials.

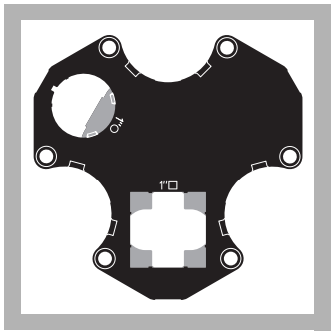
Collect the following items:	**Quantity**
Citrate Buffer Powder Pillows	1
Chloroform	500 mL
DithiVer Metals Reagent Powder Pillows	1
Lead Reagent Set	1
Potassium Cyanide	2 g
Sodium Hydroxide solution, 5.0 N	5 mL
Sodium Hydroxide Standard Solution, 5.0 N	varies
Cotton Balls	1
Clippers	1
Cylinder, 50-mL graduated mixing	1
Cylinder, 5-mL graduated	1
Cylinder, 50-mL graduated	1
Cylinder, 250-mL graduated	1
Funnel, 500-mL separatory	1
Sample Cells, 1-inch square, 25-mL	2
Spoon, measuring, 1.0-g	1
Support Ring (4-inch) and Stand (5 x 8-inch base)	1

Note: *Reorder information for consumables and replacement items is on page 6.*

Powder Pillows — Method 8033

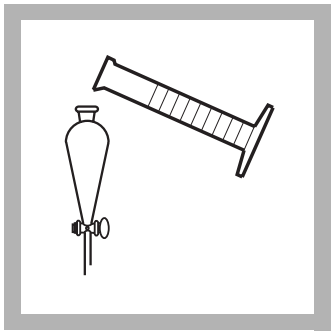
DANGER
Cyanide is a deadly poison. Use a fume hood. Maintain cyanide solutions at pH 11 or greater to prevent formation of cyanide gas.

1. Select the test.

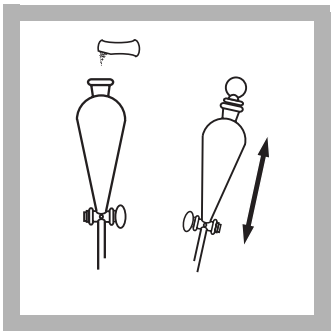


2. Insert the Multi-cell Adapter with the 1-inch square cell holder facing the user.

3. Fill a 250-mL graduated cylinder to the 250-mL mark with sample.

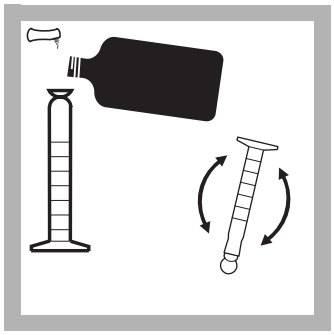


4. Transfer the sample into 500-mL separatory funnel.



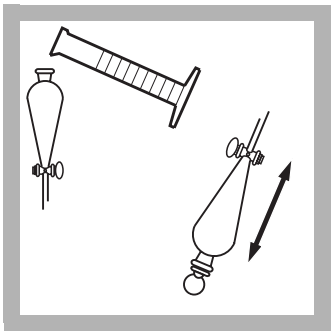
5. Add the contents of one Buffer Powder Pillow for heavy metals, citrate type.

Stopper the funnel and shake to dissolve.



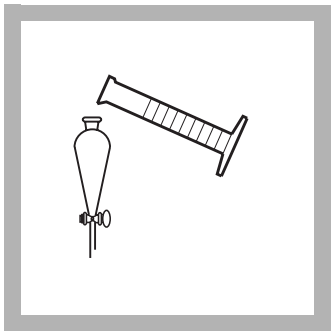
6. DithiVer Solution Preparation:
Add 50 mL of chloroform to a 50-mL mixing graduated cylinder. Add the contents of one DithiVer Metals Reagent Powder Pillow.

Stopper the cylinder. Invert several times to mix.

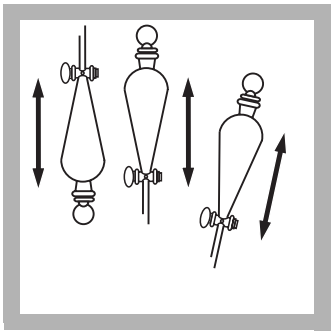


7. Measure 30 mL of the prepared dithizone solution with a second graduated cylinder and add to the separatory funnel.

Stopper and invert to mix. Open stopcock to vent. Close the stopcock.

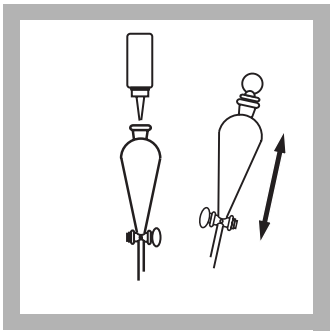


8. Add 5 mL of 5.0 N Sodium Hydroxide Standard Solution.



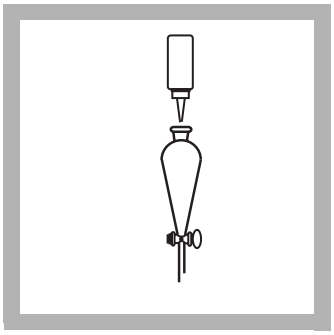
9. Stopper. Invert. Open stopcock to vent. Close the stopcock and shake the funnel once or twice and vent again.

Note: *Add a few drops of 5.25 N Sulfuric Acid Standard Solution if the solution turns orange on shaking. The blue-green color will reappear. To avoid higher blanks, repeat procedure on new sample and use less sodium hydroxide in step 8.*



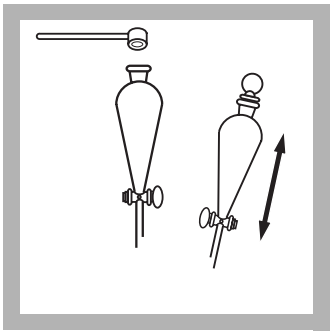
10. Continue adding 5.0 N Sodium Hydroxide Standard Solution dropwise and shaking the funnel after every few drops until the color of the solution being shaken changes from blue-green to orange.

Large amounts of zinc cause the color transition at the end point to be indistinct.



11. Add 5 more drops of 5.0 N Sodium Hydroxide Standard Solution.

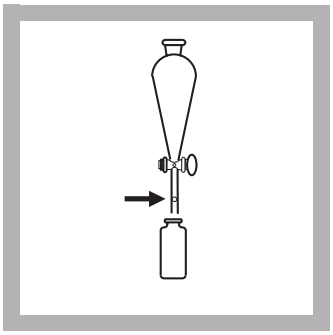
A pink color in the bottom (chloroform) layer at this point does not necessarily indicate lead is present. Only after adding the potassium cyanide in the next step will the presence of lead be confirmed by a pink color.



12. Add 2 heaping 1.0-g scoops of potassium cyanide to the funnel. Stopper.

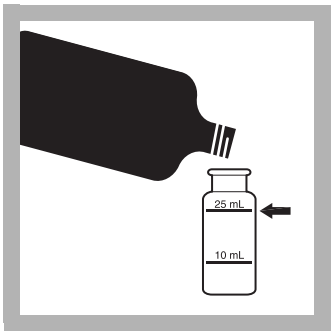
Shake vigorously until the potassium cyanide is all dissolved (about 15 seconds).

13. Wait one minute for the layers to separate. The bottom (chloroform) layer will be pink if lead is present.



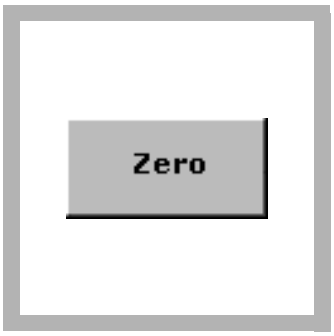
14. Prepared Sample: Insert a cotton plug the size of a pea into the delivery tube of the funnel and slowly drain the bottom (chloroform) layer into a dry 25-mL square sample cell. Stopper.

The lead-dithizone complex is stable for at least thirty minutes if the sample cell is kept tightly capped and out of direct sunlight.



15. Blank Preparation: Fill another 25-mL square sample cell with chloroform. Stopper.

16. Insert the blank into the cell holder with the fill line facing the user.



17. Press **ZERO**.

The display will show:

0 µg/L Pb^{2+}

18. Insert the prepared sample into the cell holder with the fill line facing the user. Results are in µg/L Pb^{2+}.

Interferences

Table 1 Interfering Substances and Levels

Interfering Substance	Interference Levels and Treatments
Highly buffered samples or extreme sample pH	All levels. See procedure below.
Bismuth	All levels. See procedure below.
Copper	All levels. See procedure below.
Mercury	All levels. See procedure below.
Silver	All levels. See procedure below.
Tin	All levels. See procedure below.

Table 2 Substances That Do Not Interfere

Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Calcium	Nickel
Chromium	Tin
Cobalt	Zinc
Iron	

Eliminate interference from the metals in Table 1 by the following treatment, beginning after Step 6.

1. Measure about 5-mL of the DithiVer solution into the separatory funnel. Stopper the funnel, invert and open the stopcock to vent. Close the stopcock and shake the solution vigorously for 15 seconds. Allow the funnel to stand undisturbed until the layers separate (about 30 seconds). A yellow, red, or bronze color in the bottom (chloroform) layer confirms the presence of interfering metals. Draw off and collect the bottom (chloroform) layer for proper disposal.

2. Repeat extraction with fresh 5-mL portions of prepared dithizone solution (collecting the bottom layer each time in appropriate waste collection vessel) until the bottom layer shows a pure dark green color for three successive extracts. Extractions can be repeated a number of times without appreciably affecting the amount of lead in the sample.

3. Extract the solution with several 2 or 3 mL portions of pure chloroform to remove any remaining dithizone, again collecting the bottom layer each time for proper disposal.

4. Continue the procedure, substituting 28.5 mL of prepared dithizone solution for the 30 mL in Step 7.

DithiVer Solution Preparation, Storage, and Reagent Blank

Store DithiVer Powder Pillows away from light and heat. A convenient way to prepare this solution is to add the contents of 10 DithiVer Metals Reagent Powder Pillows to a 500-mL bottle of chloroform and invert several times until well mixed (carrier powder may not dissolve). Store dithizone solution in an amber glass bottle. This solution is stable for 24 hours.

A reagent blank using deionized water should be carried out through the entire method to obtain the most accurate results.

Sample Collection, Preservation, and Storage

Collect samples in an acid-washed glass or plastic containers. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Store preserved samples up to six months at room temperature. Adjust the pH to 2.5 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions.

Accuracy Check

1. Leave the unspiked sample in the sample cell compartment. Verify that the units displayed are in µg/L.

2. Press **OPTIONS>MORE**. Press **STANDARD ADDITIONS**. A summary of the standard additions procedure will appear.

3. Press **OK** to accept the default values for standard concentration, sample volume, and spike volumes. Press **EDIT** to change these values. After values are accepted, the unspiked sample reading will appear in top row. See the user manual for more information.

4. Snap the neck off a Lead Voluette Ampule Standard, 50-mg/L Pb.

5. Use the TenSette® Pipet (do not use a glass pipet) to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively to three 250-mL samples and mix each thoroughly.

6. Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under **READ** each time. Each addition should reflect approximately 100% recovery.

7. After completing the sequence, press **GRAPH** to view the best-fit line through the standard additions data points, accounting for the matrix interferences. Press **IDEAL LINE** to view the relationship between the sample spikes and the “Ideal Line” of 100% recovery.

Standard Solution Method

1. Prepare a 10-mg/L lead standard solution by pipetting 10.00 mL of Lead Standard Solution, 100-mg/L, into a 100-mL volumetric flask.

2. Add 0.2 mL of concentrated nitric acid using a TenSette Pipet to prevent the adsorption of lead onto the container walls. Dilute to the mark with deionized water and mix thoroughly.

3. To make a 200-µg/L standard, pipet 5.00 mL of the 10.0-mg/L standard into 245 mL of deionized water in the 500-mL separatory funnel in Step 4 of the Dithizone procedure. Prepare these solutions daily. Perform the lead procedure as described above.

4. To adjust the calibration curve using the reading obtained with the standard solution, press **OPTIONS>MORE** on the current program menu. Press **STANDARD ADJUST**.

5. Press **ON**. Press **ADJUST** to accept the displayed concentration. If an alternate concentration is used, press the number in the box to enter the actual concentration, then press **OK**. Press **ADJUST**.

Method Performance

Precision
Standard: 150 µg/L Pb

Program	95% Confidence Limits of Distribution
280	140–160 µg/L Pb

Sensitivity

Portion of Curve:	∆Abs	∆Concentration
Entire Range	0.010	2.3 µg/L

Summary of Method

The dithizone method is designed for the determination of lead in water and wastewater. The DithiVer Metals Reagent is a stable powder form of dithizone. Lead ions in basic solution react with dithizone to form a pink to red lead-dithizonate complex, which is extracted with chloroform. Test results are measured at 515 nm.

Consumables and Replacement Items

Required Reagents

Description	Quantity/Test	Unit	Cat. No.
Lead Reagent Set (100 Tests)	—	—	22431-00
Includes: (1) 14202-99, (2) 14458-17, (1) 12616-99, (2) 767-14, (1) 2450-53, (2) 2450-26			
Buffer Powder Pillows, citrate	1	100/pkg	14202-99
Chloroform, ACS	30 mL	4 L	14458-17
DithiVer Metals Reagent Powder Pillows	1	100/pkg	12616-99
Potassium Cyanide	0.1 g	125 g	767-14
Sodium Hydroxide Solution, 5.0 N	5 mL	1000 mL	2450-53
Sodium Hydroxide Standard Solution, 5.0 N	varies	59 mL DB	2450-26

Required Apparatus

Description	Quantity/Test	Unit	Cat. No.
Clippers, for opening powder pillows	1	each	968-00
Cotton Balls, absorbent	1	100/pkg	2572-01
Cylinder, graduated, 5-mL	1	each	508-37
Cylinder, graduated, 50-mL	1	each	508-41
Cylinder, graduated, 250-mL	1	each	508-46
Cylinder, graduated, mixing, 50-mL	1	each	1896-41
Funnel, separatory, 500-mL	1	each	520-49
pH Meter, sens***ion***™1, portable, with electrode	1	each	51700-10
Sample Cell, 1-inch square, 25 mL with cap	2	2/pkg	26126-02
Spoon, measuring,1-g	1	each	510-00
Support Ring, 4"	1	each	580-01
Support Ring Stand, 5" x 8" base	1	each	563-00

Recommended Standards

Description	Unit	Cat. No.
Lead Standard Solution, 100 mg/L Pb	100 mL	12617-42
Lead Standard Solution, 10-mL Voluette Ampules, 50-mg/L Pb	16/pkg	14262-10

Optional Reagents and Apparatus

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Chloroform, ACS	500 mL	14458-49
Filter Discs, glass, 47 mm	100/pkg	2530-00
Filter Holder, glass, for 47-mm filter	each	2340-00
Flask, Erlenmeyer, 500-mL	each	505-49
Flask, filtering, 500-mL	each	546-49
Flask, volumetric, Class A, 100-mL	each	14574-42
Nitric Acid Solution, 1:1	500 mL	2540-49
Nitric Acid, ACS	500 mL	152-49
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	391-33
Pipet, serological, 2-mL	each	532-36
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for TenSette Pipet 19700-01	50/pkg	21856-96
Pipet, volumetric, 5.00-mL, Class A	each	14515-37
Pipet, volumetric, 10.00-mL, Class A	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Sulfuric Acid, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 liters	272-56

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